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(21) International Application Number: PCT/US98/06836 (22) International Filing Date: 7 April 1998 (07.04.98) (30) Priority Data: 08/840,961 17 April 1997 (17.04.97) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 08/840,961 (CON) Filed on 17 April 1997 (17.04.97) (71) Applicant (for all designated States except US): CREE RESEARCH, INC. [US/US]; 4600 Silicon Drive, Durham, NC 27703-8475 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): NEGLEY, Gerald, H. [US/US]; 3512 NC 86 S., Hillsborough, NC 27278 (US). (74) Agent: SUMMA, Philip; Suite 500, 5925 Carnegie Boulevard, Charlotte, NC 28209 (US).		(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: RECOVERY OF SURFACE-READY SILICON CARBIDE SUBSTRATES		
(57) Abstract A method is disclosed for recovering surface-ready silicon carbide substrates from heteroepitaxial structures of Group III nitrides on silicon carbide substrates. The method comprises subjecting a Group III nitride epitaxial layer on a silicon carbide substrate to a stress that sufficiently increases the number of dislocations in the epitaxial layer to make the epitaxial layer subject to attack and dissolution in a mineral acid, but that otherwise does not affect the silicon carbide substrate, and thereafter contacting the epitaxial layer with a mineral acid to remove the Group III nitride while leaving the silicon carbide substrate unaffected.		

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RECOVERY OF SURFACE-READY SILICON CARBIDE SUBSTRATES

Field of the Invention

The present invention relates to the manufacture
5 of semiconductor devices from wide-bandgap materials,
and in particular relates to a method of recovering
silicon carbide substrates from composite structures of
such substrates with Group III nitride epitaxial
layers.

Background of the Invention

10 The present invention relates to the recent
increase in the research, development, manufacture and
use of electronic devices made from wide-bandgap
semiconductors, specifically including silicon carbide
15 (SiC) and Group III nitrides (*i.e.*, Group III of the
Periodic Table: B, Al, Ga, In, Tl) such as gallium
nitride (GaN). Both of these materials have generated
such interest for several reasons. Silicon carbide is
an attractive candidate material for semiconductor
20 applications because of its wide bandgap (2.99 eV for
alpha-SiC at 300K) and its other exceptional
electronic, physical, thermal and chemical properties.

Gallium nitride, although not sharing all of the
same physical properties as silicon carbide offers the
25 electronic advantage of being a wide-bandgap (3.36 eV
at 300K) directtransition emitter. Stated somewhat
differently, both silicon carbide and gallium nitride
are ideal candidate materials for producing light
emitting diodes (LEDs) that because of their wide
30 bandgaps, are capable of emitting at higher energies.

In terms of the characteristics of light, higher energy represents higher frequencies and longer wavelengths. In particular, gallium nitride and silicon carbide have bandgaps sufficiently wide to allow them to emit light
5 in the blue portion of the visible spectrum (i.e., wavelengths of between about 455 and 492 nanometers, nm), a color that cannot be directly produced by most other semiconductor materials. A thorough discussion of optoelectronic devices, and their design, the theory
10 behind their operation, is set forth in Sze, *Physics of Semiconductor Devices*, (1981), and particularly in Chapter 12, pages 681-742, with related discussions of photodetectors in Chapter 13 (page 743) and solar cells in Chapter 14 (page 790). Such background and theory
15 will not be discussed further herein other than as necessary to describe the present invention.

In brief, however, silicon carbide is an indirect emitter, which means that a portion of the energy generated by each transition is generated as
20 vibrational energy rather than as emitted light. In comparison, gallium nitride is a direct emitter in which all of the energy generated by a transition is emitted as light. Thus, at any given current input, gallium nitride offers the possibility for more
25 efficient LEDs, than does silicon carbide. To date, however, gallium nitride has not been produced in bulk crystal form, and thus in order to form an LED or other optoelectronic device from gallium nitride, epitaxial layers of gallium nitride must be formed on some
30 suitable substrate material.

Conventionally, sapphire has been the preferred substrate material for gallium nitride because of its physical properties and because of the generally satisfactory crystal lattice match between gallium
5 nitride and sapphire (Al_2O_3). Sapphire cannot be made electronically conductive, however, and thus the physical geometry of LEDs formed from gallium nitride epitaxial layers on sapphire substrates are typically of the "same side" variety rather than the generally
10 more preferred "vertical" LED geometry. As used herein, the term "vertical" refers to an LED in which the ohmic contacts can be placed on opposite faces of the device rather than on a common face.

Accordingly, and in addition to its own
15 advantageous electronic properties, silicon carbide provides an excellent substrate material for gallium nitride and other Group III nitride devices. Accordingly, many recent advances in the production of blue LEDs have been based upon a combination of such
20 gallium nitride epitaxial layers on silicon carbide substrates.

Although the manufacture of such GaN-SiC devices has progressed rapidly, epitaxial growth of such materials such as gallium nitride on silicon carbide
25 continues to represent a complex process, and one in which a substantial proportion of attempts produce device precursors that are unsatisfactory for one or more reasons.

More particularly, a GaN on SiC LED typically
30 consists of an SiC substrate with a back ohmic contact,

one or more buffer layers on the SiC substrate that provide a crystal lattice transition between the SiC and the GaN, and at least two epitaxial layers of gallium nitride on the buffer layer. The gallium
5 nitride layers include at least one p-type layer and one n-type layer adjacent one another to form the p-n junction of the device. A top ohmic contact is usually made to the top layer of gallium nitride, or in some cases to another material that for some other desired
10 reason forms the top layer of the device.

As well known to those of ordinary skill in this industry, semiconductor substrates are typically sliced from bulk crystals in the form of circular disks, generally referred to as "wafers," upon which various
15 other layers, such as epitaxial layers of GaN, are formed. Because the bulk growth of silicon carbide and the preparation of silicon carbide wafers are both processes which represent significant technical challenge and economic investment, the wafers are in
20 turn quite valuable. If, however, after the gallium nitride epitaxial layers are grown on the SiC wafer, they are found to be defective, or simply unsatisfactory from a desired quality standpoint, the entire wafer becomes a waste product.

25 Thus, a need exists for removing gallium nitride from silicon carbide in a manner that preserves the silicon carbide wafer. Interestingly enough, the recent success of high quality epitaxial growth of gallium nitride on silicon carbide has exacerbated this
30 problem. Namely, the high quality gallium nitride (and

other Group III nitride) epitaxial layers required to produce appropriate LEDs, are similarly much more resistant to the normal techniques (typically wet or dry etching) used to remove unwanted material in conventional semiconductor processes.

Object and Summary of the Invention

Therefore, it is an object of the present invention to provide a method of recovering surface-ready silicon carbide substrates from heteroepitaxial structures of Group III nitrides on silicon carbide substrates, particularly when the Group III nitride layers are high quality crystalline materials.

The invention meets this object with the method of recovering such substrates by subjecting a Group III nitride epitaxial layer on a silicon carbide substrate to a stress that sufficiently increases the number of dislocations in the epitaxial layer to make the epitaxial layer subject to attack and dissolution in a mineral acid, but that otherwise does not affect the silicon carbide substrate, and thereafter contacting the epitaxial layer with a mineral acid to remove the Group III nitride while leaving the silicon carbide substrate unaffected.

Detailed Description

The invention is a method of recovering surface-ready silicon carbide substrates from heteroepitaxial structures of Group III nitrides on silicon carbide substrates. The method comprises subjecting the Group III nitride epitaxial layer on a

silicon carbide substrate to a stress that sufficiently increases the number of dislocations in the epitaxial layer to make the epitaxial layer subject to attack and dissolution in a mineral acid, but that otherwise does not affect the silicon carbide substrate. Thereafter, the epitaxial layer is contacted with a mineral acid to remove the Group III nitride while leaving the silicon carbide substrate unaffected.

Because gallium nitride is the most commonly used Group III nitride for LEDs, the specification will often refer to gallium nitride. It will be understood, however, that the invention embraces all of the Group III nitrides described above, including binary, ternary, and tertiary nitrides. Such binary nitrides also include aluminum nitride (AlN) and indium nitride (InN). Ternary nitrides include those often referred to as "aluminum gallium nitride," and which are typically designated by the empirical formula $\text{Al}_x\text{Ga}_{1-x}\text{N}$. It will be understood that this general formula is used to refer to a variety of aluminum gallium nitride compounds that are in many ways similar, but that differ according to the atomic fractions of aluminum and gallium, with somewhat differing properties as well.

Tertiary Group III nitrides refer for example to indium aluminum gallium nitride, which is similarly designated $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$. The reasons for using gallium nitride, aluminum, Y gallium nitride, or other ternary or tertiary nitrides are set forth in exemplary, but certainly not limiting, fashion in U.S. Patent No.

5,523,589; 5,592,501; and 5,739,554; all of which are commonly assigned with the present invention.

Although the inventors do not wish to be bound by any particular theory of the invention, it appears that recent successes in the crystal growth of Group III nitrides on silicon carbide has produced high-quality Group III nitride layers whose crystal structure is less susceptible to wet chemical attack than are Group III nitride layers produced by other techniques. Thus, although in one sense gallium nitride and other Group III nitrides have been recognized as being susceptible to wet chemical etch, the higher quality Group III nitrides produced more recently are not so susceptible. Accordingly, it appears that these higher quality gallium nitride epitaxial layers must be physically brought to a lower quality ("the stress step") before they can be successfully attacked with a wet chemical etch such as a mineral acid.

Furthermore, it will be understood that the crystal defects referred to herein, although frequently labeled as "dislocations," include, but are not limited to, slips, edge dislocations, and screw dislocations.

Accordingly, in preferred embodiments of the invention, there are several techniques for applying the stress.

A first technique is to raise the temperature of the substrate and the epitaxial layers to a temperature sufficient to dissociate the gallium nitride. In more preferred embodiments, this technique comprises heating the substrate and epitaxial layers to temperatures of

about 1000°C in the presence of oxygen or argon. The equipment used for these heating steps is otherwise conventional in this art, and can be used to practice the invention without undue experimentation.

5 In another embodiment, the stress step comprises exposing the substrate and epitaxial layers to rapid thermal annealing (RTA). As used herein, rapid thermal annealing refers to the technique generally well understood in the semiconductor arts in which an item
10 such as a semiconductor material is placed in a device that, because of its physical capabilities, can raise the temperature of the semiconductor material very quickly; i.e., on the order of about 10°C per second. Again, although not wishing to be bound by any
15 particular theory, it appears that when the lattice mismatch between the gallium nitride and silicon carbide (even in the presence of a buffer layer) is subjected to such rapid thermal stress (which is not expected in any ordinary use of the device), the
20 mismatch creates or increases the number of defects in the crystal, particularly dislocation defects, that permit the mineral acid to attack and remove the Group III nitride.

In some embodiments, the rapid thermal annealing
25 is carried out at relatively low pressure (e.g., about 10^{-6} torr), while in other circumstances, the rapid thermal annealing can be carried out in an ambient atmosphere (air) at high temperatures (e.g., 1050°C).

In yet another embodiment, the step of subjecting
30 the Group III nitride layer to stress can comprise

physically abrading the layer, for example by bombarding it with silicon carbide or aluminum oxide powders. It presently appears, however, that such physical abrasion methods may cause underlying damage
5 to the silicon carbide substrate as well, which is a less desirable result.

In the preferred embodiments of the method, the step of contacting the epitaxial layer with a mineral acid comprises contacting the layer with phosphoric
10 acid (H_3PO_4). Most preferably 85% H_3PO_4 , heated to about $170^\circ C$ is used to remove the nitride epitaxial layers. In a preferred embodiment, the etching apparatus comprises a quartz beaker and a Wollam condenser. The condenser keeps the H_3PO_4 solution at 85% by preventing
15 water from evaporating.

As noted above, the difficulty in removing the gallium nitride from the substrate relates back to the quality of the gallium nitride epitaxial layer, which in turn relates back to the method by which it is
20 produced. Thus, in another aspect, the invention comprises the step of depositing the Group III nitride epitaxial layer on the substrate prior to the step of subjecting the layer to stress. More particularly, it has been found that electronically high quality Group
25 III nitride epitaxial layers, and thus those hardest to remove, tend to be produced by metal organic chemical vapor deposition (MOCVD), and are typically of higher quality than those produced by vapor phase epitaxy (VPE). Although these processes are to a great extent
30 similar, as used herein, vapor phase epitaxy refers to

processes such as those in which a gas (such as a blend of hydrogen chloride and hydrogen) is bubbled through liquid gallium to produce a gallium chloride vapor, which is then directed to react with a nitrogen
5 containing gas, typically ammonia (NH_3), to form gallium nitride. Some VPE processes seem to inherently form dislocations and tend to capture chloride atoms or chloride ions in the resulting material.

Alternatively, MOCVD uses a metal organic compound
10 (in which the Group III element is the metal) in the vapor phase. To some extent, the vapor phase compound will dissociate to form metal radicals. These radicals in turn react with the nitrogen containing gas (again typically ammonia) to form the Group III nitride.
15 Trimethyl gallium ("TMG," $(\text{CH}_3)_3\text{Ga}$) is a preferred metal organic source for gallium.

Thus, in the present invention the step of depositing the Group III nitride epitaxial layer on the silicon carbide substrate preferably comprises MOCVD.
20 In turn, the MOCVD is preferably carried out from a vapor phase reaction between an organic Group III compound such as TMG, and ammonia (NH_3).

It will be understood, however, that the invention is not limited by the method in which the Group III
25 nitride layers are deposited. Other appropriate methods can include (but are not limited to) molecular beam epitaxy (MBE), the aforementioned VPE, and liquid phase epitaxy (LPE).

It has also come to be recognized in recent years
30 that an appropriate buffer layer or layers positioned

between the silicon carbide substrate and the gallium nitride epitaxial layers can greatly improve the quality of those epitaxial layers. Thus, a preferred embodiment of the present invention further comprises
5 depositing such a buffer layer on the silicon carbide substrate prior to the step of depositing the Group III nitride epitaxial layers. Appropriate buffer layers are described in several of the patents already cited as well in U.S. Patent No. 5,393,993, which is commonly
10 assigned with the present invention, and which is incorporated entirely herein by reference. The method of the invention removes these buffer layers as well.

In summary, the invention produces a silicon carbide wafer that is otherwise indistinguishable from
15 wafers that have never carried Group III nitride epitaxial layers. Such recovered wafers can accordingly be used or processed in the same manner as "new" wafers, thus offering significant gains in the efficiency and economy of wafer and device production.

20 In the specification, there have been set forth preferred and exemplary embodiments, which have been included by way of example and not limitation, the scope of invention being set forth in the following claims.

CLAIMS:

1. A method of recovering surface-ready silicon
carbide substrates from heteroepitaxial structures of
5 Group III nitrides on silicon carbide substrates by
chemically removing the nitrides from the substrates;
characterized by:

subjecting a Group III nitride epitaxial layer on
a silicon carbide substrate to a stress that
10 sufficiently increases the number of dislocations in
the epitaxial layer to make the epitaxial layer subject
to attack and dissolution in a mineral acid, but that
otherwise does not affect the silicon carbide
substrate; and

15 thereafter contacting the epitaxial layer with a
mineral acid to remove the Group III nitride while
leaving the silicon carbide substrate unaffected.

2. A silicon carbide substrate produced by the
20 method of Claim 1.

3. A method according to Claim 1 wherein the step
of subjecting the Group III nitride layer to stress
comprises subjecting a layer of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ to stress.
25

4. A method according to Claim 1 wherein the step
of subjecting the Group III nitride layer to stress
comprises subjecting a gallium nitride layer to stress.

5. A method according to Claim 1 wherein the stress step comprises heating the substrate and epitaxial layer to a temperature sufficient to cause the epitaxial layer to dissociate.

5

6. A method according to Claim 1 wherein the stress step comprises subjecting the substrate and epitaxial layer to rapid thermal annealing.

10

7. A method according to Claim 6 wherein the rapid thermal annealing is carried out at low pressure.

8. A method according to Claim 6 wherein the rapid thermal annealing is carried out in an ambient atmosphere at high temperature.

15

9. A method according to Claim 1 wherein the step of contacting the epitaxial layer with a mineral acid comprises contacting the layer with hot concentrated phosphoric acid.

20

10. A method according to Claim 1 wherein the step of subjecting the Group III nitride layer to stress comprises physically abrading the layer.

25

11. A method according to Claim 1 and further comprising the step of depositing the Group III nitride epitaxial layer on the substrate prior to the step of subjecting the layer to stress.

12. A method according to Claim 11 wherein the step of depositing the Group III nitride epitaxial layer on the silicon carbide substrate comprises metal organic chemical vapor deposition.

5

13. A method according to Claim 12 wherein the step of depositing the Group III nitride epitaxial layer on the silicon carbide substrate comprises depositing the Group III nitride from a vapor phase reaction between an organic Group III compound and ammonia.

10

14. A method according to Claim 12 wherein the step of depositing the Group III nitride epitaxial layer on the silicon carbide substrate comprises depositing gallium nitride from a vapor phase reaction between trimethyl gallium and ammonia.

15

15. A method according to Claim 11 wherein the step of depositing the Group III nitride epitaxial layer on the silicon carbide substrate further comprises depositing a buffer layer on the silicon carbide substrate prior to the step of depositing the Group III nitride epitaxial layer.

20

25

16. A method according to Claim 11 wherein the step of depositing the Group III nitride layer comprises depositing a layer of $\text{Al}_x\text{Ga}_{1-x}\text{N}$.

17. A method according to Claim 11 wherein the stress step comprises heating the substrate and epitaxial layer to a temperature sufficient to dissociate the epitaxial layer.

INTERNATIONAL SEARCH REPORT

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PCT/US 98/06836

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01L33/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HUGHES W C ET AL: "Reactive ion etching of AlN, AlGa _N , and GaN using BC ₁ /sub 3/" GALLIUM NITRIDE AND RELATED MATERIALS. FIRST INTERNATIONAL SYMPOSIUM, GALLIUM NITRIDE AND RELATED MATERIALS. FIRST INTERNATIONAL SYMPOSIUM, BOSTON, MA, USA, 27 NOV.-1 DEC. 1995, 1996, PITTSBURGH, PA, USA, MATER. RES. SOC, USA, pages 757-762, XP002072134 see abstract	1, 11, 12, 16
A	HIDENAO TANAKA ET AL: "REACTIVE FAST ATOM BEAM ETCHING OF A WIDE-GAP SEMICONDUCTOR GAN" OPTOELECTRONICS DEVICES AND TECHNOLOGIES, vol. 6, no. 1, 1 June 1991, pages 150-153, XP000245832 see the whole document	1, 9, 11-14

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

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